BIOPETROL SYNTHESIZED FROM RUBBER SEED OIL BY ZEOLITE CATALYST: EFFECT OF ETHANOL IN SOLVENT EXTRACTION OF RUBBER SEEDS

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ABSTRACT

Currently, most of the bio-petrol is produced from the refined or edible type oils such as the utilization of palm oil for the production of more environmental friendly bio-fuels. However, by extracting rubber seed oil (RSO) from the rubber seeds, this method is more favorable as the RSO contains more fatty acid to be produced into bio-petrol. The rubber seeds are readily available, cheap and help to improve the socioeconomic issues. The RSO is extracted using the Soxhlet Extraction method. The cleaned, shelled and milled rubber seeds are placed into a thimble in the main chamber of the extractor. The solvent ethanol in the receiving flask is left to boil until it vaporizes and condensed, filling up the main chamber, extracting the RSO from the rubber seeds. The catalytic cracking of the mixture of 0.1L of RSO, 20g of catalyst and bumping chips at 300^0C for 45 minutes using Zeolite catalyst is to boost up the rate of reaction so that more successful reactions between the reactant particles can occur. The presence of Isooctane in a sample detected using Gas Chromatogram indicating that bio-petrol can be produced. Standards of different ratio mixtures of hexane and Isooctane were used to obtain chromatograms for Isooctane until a calibration curve is plotted from which the Isooctane produced can be determined. The results show that the actual concentration of Isooctane is very big. This could be explained using the cause of interlayer spacing of catalyst structure, larger surface area for reactions to occur, various types of fatty acid mixture present in RSO, the incorrect chromatogram modifications and the contamination in RSO. The mass of catalyst and volume of RSO used will affect the percentage of concentration of Isooctane in samples. As a conclusion, Bio-petrol can be produced from RSO using Zeolite catalyst in the catalytic cracking process.

ABSTRAK

Pada masa kini, kebanyakkan bio-petrol dihasilkan daripada minyak tumbuh-tumbuhan yang boleh dimakan contohnya seperti minyak pokok kelapa sawit kerana bio-petrol yang dihasilkan mengunakan mempunyai ciri-ciri mesra alam. Dengan mengekstrak minyak biji getah dari biji getah kita akan mempunyai minyak yang mengandungi kandungan acid lemak yang tinggi yang boleh diproses untuk dijadikan kepada bio-petrol. Biji-biji getah sangat mudah diperolehi dan harganya adalah amat murah. Minyak biji getah diekstrek mengunakan kaedah Soxhlet. Biji getah yang dibersih, dikupas kulitnya dan dikisar dimasukkan ke dalam timble yang kemudian diletak di ruang utama Soxhlet ekstraktor. Pelarut Etanol dalam kelalang penerima dibiarkan mendidih sehinggalah ia menyejat dan mengisi ruang utama dan mengekstrak minyak biji getah dari benih getah. 0.1L minyak biji getah dicampur dengan 20g pemangkin zeolite dan dipanaskan pada suhu 300^0C selama 45 minit. Pemangkin zeolite digunakan adalah untuk meningkatkan kadar tindak balas antara zarah-zarah. Kehadiran Isooctane dalam sampel dikesan menggunakan Kromatogram Gas dan inin menunjukkan bahawa bio-petrol dapat dihasilkan menggunakan minyak benih getah. Standard campura nisbah yang berbeza hexane dan Isooctane telah digunakan untuk mendapatkan kromatogram untuk Isooctane sehingga keluk penentukuran diplotkan hasil daripada kepekatan Isooctane yang dihasilkan. Keputusan menunjukkan bahawa kepekatan sebenar Isooctane adalah sangat besar. Hal ini disebabkan oleh minyak sample yang tidak larut sepenuhnya dalam pelarut hexane, keretakan dan pengisomeran rawak semasa proses keretakan rantai hydrocarbon dengan menggunakan pemangkin dan pencemaran minyak benih getah. Jumlah isipadu pelarut yang digunakan akan mempengaruhi peratus kepekatan Isooctane dalam sampel. Kesimpulannya, bio-petrol dapat dihasilkan daripada minyak benih getah dengan menggunakan zeolite sebagai pemangkin.

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LIST OF SYMBOLS

P	-	Pressure
m	-	Mass
ΔH	-	Enthalpy change of reaction
ΔS	-	Entropy change of reaction
ΔG	-	Energy change of reaction
T	-	Temperature
ρ	-	Density
μ	-	Viscosity of liquid (Pa.s)
h	-	Heat transfer coefficient
^{o}C	-	Degree Celsius
kg	-	Kilogram
K	-	Degree Kelvin
m	-	Meter
L	-	Liter

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Environmental pollution is the greatest treat which is faced by the world in these modern times. Environmental pollution is defined as the introduction of contaminants into an environment that causes instability, disorder, harm or discomfort to the ecosystem. There are many factors which contribute to the current pollution level of the world and one of the major factors is combustion of fossil fuels. Fossil fuels are defined as any carbon-containing fuel derived from the decomposed remains of prehistoric plants and animals. Some of the examples of fossil fuels are coal, petroleum and natural gas. Combustion of fossil fuel produces a very high amount of carbon dioxide. The high concentration of carbon dioxide in the atmosphere is the prime factor for today's global warming phenomena.

Today the accessible oil reservoirs which are the major sauce of the fossil fuels are gradually depleting , it is very important to develop an appropriate long-term strategies based on the utilization of the renewable fuel that will gradually substitute the depleting fossil fuel production (Westermann et. 2007). So it has become a top priority for developing or developed countries to find a sustainable fuel which is cheap and easy to

mass produce. One of the major solutions to overcome the problem is by using bio-petrol or the alternative petrol as a renewable and biodegradable type of fuel.

The bio-petrol is majorly used in transportation sector. Bio-petrol or biomass is produced from plants or from agricultural waste. The ethanol production for transport fuel tripled between 2000 and 2007 from 17 billion to more than 52 billion liters, while biodiesel expanded eleven-fold from less than 1 billion to almost 11 billion liters. Altogether bio-fuels provided 1.8% of the worlds transport fuel. Recent estimate indicate a continued high growth. From the time frame of 2007 to 2008 the share of ethanol in global gasoline type fuel use was estimated to increase from 3.78% to 5.46% and the share of biodiesel in global diesel type fuel use from 0.93% to 1.5%.

So from the numbers above it is positive that many countries have agreed that bio-fuel production is the relevant choice to solve the depleting oil reserve problem. Bio-fuels do poses several advantages compare to fossil fuel. Those advantages are renewability, sustainability, common availability, reduction of greenhouse gases emission and its biodegradability.

The saturated fatty acids contain high potential long hydrocarbon chain alkanes which are perfect for making petrol. By using thermal cracking process the fatty acid in the rubber seeds will be broken so that it can be used to produce bio-petrol. The thermal cracking its self doesn't produce sufficient amount of product so a homogenous catalytic cracking is used to break up the large oil molecules into small molecules which will increase the rate of reaction between the liquid fatty acid and the solid catalyst.

The solid catalyst which will be used in this case is zeolite. The zeolite has been chosen due its quality of being a good absorbent.

1.2 Research Background

Finding a proper substituent for the depleting fossil fuel has become an important research now days. Various researches have been made so that a cheap and sustainable energy source can be found so that we could match up with the increasing demand for fuel. Production of bio-petrol not only matches up with the cheap and sustainable energy criteria but it also able to reduce the pollution towards the environment. Based on the research of production of bio-diesel from rubber seeds done by Department of Mechanical Engineering, National Institute of Technology Calicut, the rubber seed oil has high amount of free fatty acid. The free fatty acid content of unrefined rubber seed oil was about 17%. From the journal of A.S RAMADAS 2004 it has been stated that rubber seed kernels (50% – 60% of seed) contain 40% – 50% of brown color oil. It also has been stated that in its natural form the rubber seed oil has high acidic functional groups such as ester, methylene, terminal methyl and glyceryl.

1.3 Problem Statement

Nowadays fossil fuel price has become a crucial factor which will determine the prices of other goods in the market. It can be said that the price of fuel is proportional to the prices of the goods. So if the price of the fuel increases the prices of other products in the market will also increase. Today the price of the fuel is not at a fixed position and it is keeping on increasing due to the fact of depleting oil reserves. This scenario currently occurs not only in Malaysia, but also involving all other countries in the world. Figure 1.1 proves this scenario occurrence in United States of America.

As an example in Malaysia only, the price of Malaysia petrol has been raise by over 40% in the year 2008. The price for petrol stood at RM 2.70 a liter, an increase of 78 sen while the price of diesel was shot up by RM 1.00 at RM 2.58. Although the prices were reduced to RM 2.15 for petrol and RM 2.50 for diesel by the following month but it was estimate that there will be increase in fuel prices in the following years.

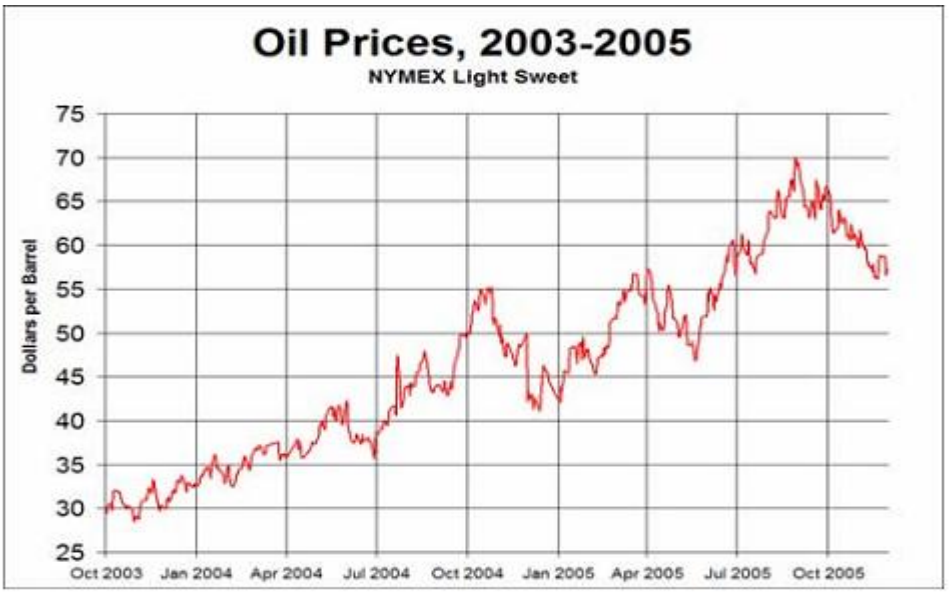

Figure 1.1: New York Mercantile Exchange

Increase in fuel prices would not be a problem if the income of the people does increase according to the fuel prices. But people's salaries will not be increased according to the increase of fuel price. So ordinary people have to bear a higher living cost with the same amount of salary. Production of bio-fuel can prevent this whole scenario from happening. Bio-fuel is better than the fossil fuel from the aspect of production cost because it would not be needed to drill deep into the earth and build factories to refine bio-fuel comparing with fossil fuels those should be refined first. Another factor which makes the bio-fuel to cost less than the fossil fuel is that the source for producing bio-fuel which are plants and agricultural waste are cheap and easy to get whereas on the other hand it is becoming difficult to find new oil reserves. So the rareness of the oil reserves makes the price for fossil fuel go sky high.

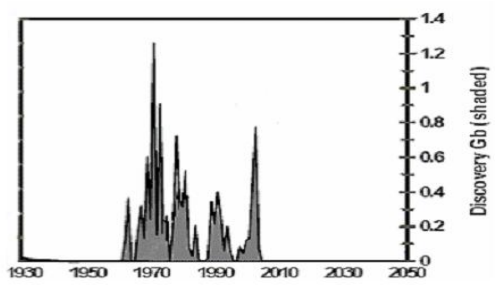

Figure 1.2: Annual Malaysian Discovery of Oil

Based on the Figure 1.2 the most amount of fossil fuel was discovered during the year 1973 and the discoveries of fossil fuel in the years that follows it always seems to be less than the amount in the year 1973. Many reasons can be stated for the short comings of the years after 1973 such as efforts for discovering new oil reserves at minimum level and instruments for discovering fossil fuel were not updated for the modern day standard. Although many reasons can be given for the situation above but the fact that cannot be ignored is the cold hard truth which is Malaysia's oil reserves are running out of fuel. The situation gets even worse when the demand for fuel increases on year by year basis as shown in Figure 1.3 below.

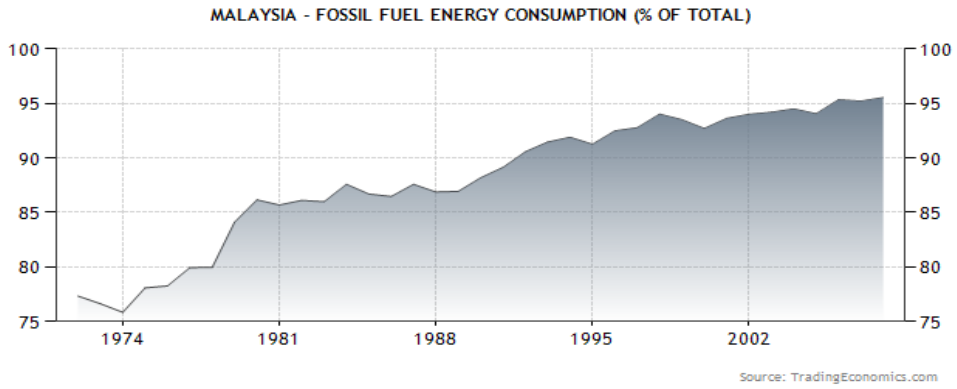

Figure 1.3: Malaysia - Fossil Fuel Energy Consumption

Limited recourses with increasing demand will only spell total chaos. To overcome this problem a lot of fuel sources in a small amount of time is required to be explored. So it is needed to discover more and more fuel reserves to satisfy the market demand. But the problem is even though the effort to find fossil fuel reserves is doubled, only a limited

number of fossil fuel reserves could be found because fossil fuel only can be formed after millions of years. So an alternative way is needed to produce fuel in a large quantity in a minimum amount of time. So the best alternative way is producing bio-fuels.

Bio-fuel is a renewable energy because it is produced from plants which are also renewable bio-organic materials. So it can be simply concluded that the bio-fuel would not diminish as long there are bio-mass. Another advantage of bio-fuel is it is biologically degradable and it will never pollute the environment.

One of the major side effects when it comes to the combustion of fossil fuels is the incomplete combustion between the mixture and the low ranking fuels. When fossil fuels burn efficiently in an excess of air or oxygen the only products are carbon dioxide and water for an example:

Examples of complete combustion burning are:

- Methane + oxygen ==> carbon + water

  $CH_{4\,(g)} + O_{2(g)} ==> C_{(s)} + 2H_2O_{(l)}$

- pentane + oxygen ==> water + carbon dioxide

  $C_5H_{12(g)} + 8O_{2(g)} ==> 5CO_{2(g)} + 6H_2O_{(l)}$

However, if there is not enough oxygen present to completely burn the fuel to carbon dioxide and water other products may form causing pollution and fuel inefficiency. This is referred to as incomplete combustion. The most common partially burned products are likely to be carbon-soot and deadly carbon monoxide (CO), as shown in Figure 1.4. Carbon-soot, a fine black powder-dust is potentially harmful and readily formed in fires and it's classically produced by smoky yellow flames. The soot, like any fine solid 'dust' is harmful when absorbed on the sensitive tissue of the linings of the nose, throat and lungs. Soot deposits cause coughing and sore throat and are ejected from your body through sneezing, coughing, and nose blowing. Coarse particles (10 microns) are inhaled into your

windpipe and settle there, causing irritation and more coughing. Soot is also a 'carrier' of polycyclic aromatic hydrocarbons (PAH's) on it which are carcinogenic. Even very low concentrations of carbon monoxide (CO) can be fatal. Oxygen is carried around the body by a complicated protein molecule in red blood cells called hemoglobin. The bonding between oxygen and hemoglobin is quite weak to allow easy oxygen transfer for cell respiration. Unfortunately, the bonding between carbon monoxide and hemoglobin is stronger, so oxygen is replaced by carbon monoxide and blocks normal cell respiration. The consequences are reduced blood oxygen concentration leading to unconsciousness and eventually death.

Figure 1.4: Percentage of Carbon Monoxide Release Test

The rubber tree (*Hevea brasiliensis*) is a plantation crop which is originated from South America and commercially cultivated around Southeast Asia in the year 1876. Every hector or rubber plantation will yield 100 to 150 kg of rubber seeds. The rubber seeds have

43% oil in composition (Nwokolo et al 1988). Rubber seed oil is a semi-dried substance (Aigbodin & Pillai 2000) that does not contain any unusual fatty acid but it is a rich source of polyunsaturated fatty acids $C_{18:2}$ and $C_{18:3}$ that makes up 52% its total fatty acid composition (Ghandhi et al 1990). Malaysia is an ideal country to start the mass production of bio-petrol from rubber seeds because Malaysia produces almost 20% of the world's natural rubber. A good deal of Malaysia's rubber comes from thousands of privately owned plots of land called small holdings, which are usually about 2 hectares. The rest is grown on big estates owned by various companies; each can cover over a thousand hectares. Altogether, Malaysia has 1.7 million hectares of rubber. So with millions of hectares of rubber plantation it's very to obtain the rubber seeds.

Table 1.1: Properties of Vegetable oil [Knothe G., R.O. Dunn and M.O. Bagby, 1998. Biodiesel: the use of vegetable oils and their derivatives as alternative diesel fuel.]

Property	Rubber seed oil	Sunflower oil	Rapeseed oil	Cotton seed oil	Soybean oil
Fatty acid composition (%)					
(i) Palmitic acid $C_{16:0}$	10.2	6.8	3.49	11.67	11.75
(ii) Stearic acid $C_{18:0}$	8.7	3.26	0.85	0.89	3.15
(iii) Oleic acid $C_{18:1}$	24.6	16.93	64.4	13.27	23.26
(iv) Linoleic acid $C_{18:2}$	39.6	73.73	22.3	57.51	55.53
(v) Linolenic acid $C_{18:3}$	16.3	0	8.23	0	6.31
Specific gravity	0.91	0.918	0.914	0.912	0.92
Viscosity (mm^2/s) at 40 °C	66.2	58	39. 5	50	65
Flash point (°C)	198	220	280	210	230
Calorific value (MJ/kg)	37.5	39.5	37.6	39.6	39.6
Acid value	34	0.15	1.14	0.11	0.2

The above Table 1.1 shows the comparison of rubber seed oil to other type of oils. Based on the comparison, it can be observed that rubber seed oil poses the ideal qualities to give higher yield of bio-petrol. Rubber seed also less expensive compared to the plant oils because of its non-edible feature.

1.4 Objective

- To synthesize isooctane from the rubber seeds
- To determine the concentration of isooctane by hereterogeneous catalytic cracking of fatty acid using Zeolite

1.5 Research Scope

In order to accomplish the objectives, following are the criteria which are the scope of this research focusing on:

1) The extraction of rubber seed oil from rubber seeds by using Soxhlet Extraction
2) The usage of catalytic cracking process to crack the fatty acid complex into smaller hydrocarbon molecules.
3) Using the Gas Chromatography method to determine the concentration of Isooctane.

1.6 Rational and Significance

Below are the rationale and significance statements of synthesizing bio-petrol from rubber seed oil:

a) Bio-petrol is an environmental-friendly fuel and can reduce greenhouse gases emission.
b) Bio-petrol is a renewable source of energy and it is biodegradable.
c) The source of the bio-petrol which is rubber seed can be obtained in vast number because in Malaysia there are 1.7 million hector of rubber plantation.
d) Bio-petrol has higher oxygen levels which are from 15% to 45% while fossil fuels have none and this makes bio-petrol more useful than fossil fuel chemically.
e) Catalytic cracking provides higher conversion of hydrocarbon than thermal cracking does by lowering the activation energy of the reaction.

CHAPTER 2

LITERATURE REVIEW

2.0 Introduction

There are many types of energy in this world for an example nuclear energy, hydraulic energy, wind energy, thermal energy and geothermal energy. Every kind of energy has its source of energy and one most important source for thermal energy is fossil fuel. Fossil fuels are one of the most expensive fuel sources in the world and one of the rarest to come by. Due to its rarity and high production cost the fossil fuels price has been increasing on yearly basis.

To prevent this energy crisis alternative energy sources has been looked into so that the increasing demand for energy can be fulfilled. One of the energy sources which is on top of the list is solar energy. Solar energy is being harnessed from the sun. This energy comes in the form of radiation which makes it possible to produce solar electricity from it. The solar energy is important for all life form on earth. Solar rays are the important ingredient in photosynthesis which is an essential process to produce oxygen by plant for all living organism. Furthermore solar energy helps to grow our food, light our days, influence weather patterns and provide heat. Solar energy is harvested by using various techniques such as the use of photovoltaic panels and solar thermal collectors. Photons contained in this solar radiation make the generation of electricity from the sun's rays possible.

Another source of energy which has considered as an ideal alternative energy is geothermal energy. Geothermal energy is the heat energy which is harnessed from within the earth and the energy which has been harnessed will be used to heat water and make steam to turn generator turbines and make electricity. Earth's source of geothermal energy comes from radioactive decay of minerals, from volcanic activity, and from solar energy absorbed at the surface. The term geothermal gradient, is the difference of temperature between the core of the planet and its surface, drives a continuous conduction of thermal energy in the form of heat from the core to the surface. The heat from hot springs which is one form of geothermal energy has been used for bathing since Paleolithic times but nowadays it is better known for generating electricity. Geothermal power has many advantages to it such as cost effective, reliable, sustainable, and environmentally friendly, but it has its share of its disadvantages. Geothermal energy can be found only at tectonic plate boundaries. So for countries such as Malaysia which is situated outside the "Pacific Ring of Fire" it's hard to acquire geothermal energy.

Besides geothermal energy and solar energy there is another type of energy which shows a promising future as an alternative which is Hydropower. Hydropower is generated by using the power of moving water to drive a water turbine and a generator. The amount energy obtained is based on the height of the water level from the water outlet and the volume of water flowing out. The difference in the water level is called the as head. The amount of potential energy contain in water is proportional to the head. To deliver water to a turbine while maintaining pressure arising from the head, a large pipe called a penstock may be used. Malaysia currently has 13 dams to harness the hydro electric so it is safe to say that hydropower has a great prospect for growing in Malaysia.

Although hydropower, solar energy and geothermal have a lot of ideal qualities to become the ideal alternative energy source but the most suitable fuel source is bio-fuel. The term biofuel or biorenewable fuel (refuel) is referred to as solid, liquid or gaseous fuels that are predominantly produced from biomass (Chhetri AB *et al*., 2008). Liquid biofuels being considered world over fall into the following categories: (a) bioalcohols (b) vegetable oils and biodiesels, and (c) biocrude and synthetic oils (Demirbas A *et al*., 2008). Bio-ethanol is made from fermenting the sugar components from the plant and it is made mostly